

---

This is an electronic reprint of the original article.

This reprint may differ from the original in pagination and typographic detail.

Author(s): Boulfrad, Yacine & Lindroos, Jeanette & Wagner, Matthias & Wolny, Franziska & Yli-Koski, Marko & Savin, Hele

Title: Experimental evidence on removing copper and light-induced degradation from silicon by negative charge

Year: 2014

Version: Final published version

**Please cite the original version:**

Boulfrad, Yacine & Lindroos, Jeanette & Wagner, Matthias & Wolny, Franziska & Yli-Koski, Marko & Savin, Hele. 2014. Experimental evidence on removing copper and light-induced degradation from silicon by negative charge. Applied Physics Letters. P. 3. 1077-3118 (electronic). DOI: 10.1063/1.4901533

Note: Copyright 2014 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.  
<http://scitation.aip.org/content/aip/journal/apl>

---

All material supplied via Aaltodoc is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

## Experimental evidence on removing copper and light-induced degradation from silicon by negative charge

Yacine Boulfrad, Jeanette Lindroos, Matthias Wagner, Franziska Wolny, Marko Yli-Koski, and Hele Savin

Citation: [Applied Physics Letters](#) **105**, 182108 (2014); doi: 10.1063/1.4901533

View online: <http://dx.doi.org/10.1063/1.4901533>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/105/18?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Preventing light-induced degradation in multicrystalline silicon](#)

J. Appl. Phys. **115**, 154902 (2014); 10.1063/1.4871404

[Light-induced hydrogen evolution from hydrogenated amorphous silicon: Hydrogen diffusion by formation of bond centered hydrogen](#)

J. Appl. Phys. **115**, 073503 (2014); 10.1063/1.4865166

[Role of copper in light induced minority-carrier lifetime degradation of silicon](#)

Appl. Phys. Lett. **95**, 152111 (2009); 10.1063/1.3250161

[Electronic characterization and effects of light-induced degradation on hydrogenated nanocrystalline silicon](#)

Appl. Phys. Lett. **88**, 071920 (2006); 10.1063/1.2175480

[Evidence for proton motion in the recovery of light-induced degradation in amorphous silicon solar cells](#)

J. Appl. Phys. **83**, 1726 (1998); 10.1063/1.366902

---



# Experimental evidence on removing copper and light-induced degradation from silicon by negative charge

Yacine Boulfrad,<sup>1,a)</sup> Jeanette Lindroos,<sup>1</sup> Matthias Wagner,<sup>2</sup> Franziska Wolny,<sup>2</sup> Marko Yli-Koski,<sup>1</sup> and Hele Savin<sup>1</sup>

<sup>1</sup>Department of Micro and Nanosciences, Aalto University, Tietotie 3, 02150 Espoo, Finland

<sup>2</sup>SolarWorld Innovations GmbH, Berthelsdorfer Str. 111A, 09599 Freiberg, Germany

(Received 15 October 2014; accepted 28 October 2014; published online 7 November 2014)

In addition to boron and oxygen, copper is also known to cause light-induced degradation (LID) in silicon. We have demonstrated previously that LID can be prevented by depositing negative corona charge onto the wafer surfaces. Positively charged interstitial copper ions are proposed to diffuse to the negatively charged surface and consequently empty the bulk of copper. In this study, copper out-diffusion was confirmed by chemical analysis of the near surface region of negatively/positively charged silicon wafer. Furthermore, LID was permanently removed by etching the copper-rich surface layer after negative charge deposition. These results demonstrate that (i) copper can be effectively removed from the bulk by negative charge, (ii) under illumination copper forms a recombination active defect in the bulk of the wafer causing severe light induced degradation.

© 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4901533>]

Low-resistivity boron-doped Czochralski silicon (Cz-Si) suffers from minority carrier recombination lifetime degradation when exposed to light. This phenomenon is known as light-induced degradation (LID), and it leads to a significant reduction of the solar cell efficiency. LID is commonly attributed to recombination-active metastable boron-oxygen complexes (BO-LID).<sup>1</sup> This degradation can be fully recovered by annealing in dark at 200 °C for 10 min, during which BO complexes are transformed to a metastable inactive state.<sup>2</sup>

Nevertheless, low levels of copper (often resulting from unintentional contamination) has also been observed to induce similar lifetime degradation upon illumination (Cu-LID).<sup>3</sup> Under illumination, the electrostatic repulsion is proposed to decrease between positively charged interstitial copper ions ( $\text{Cu}_i^+$ ) and copper precipitates,<sup>4</sup> consequently enhancing copper precipitation and considerably decreasing the electrical performance/quality of the silicon material. Copper precipitates have a strong detrimental effect on p-type silicon performance compared to  $\text{Cu}_i^+$ ,<sup>5</sup> because they form a defect band close to the middle of the silicon bandgap.<sup>6</sup> Moreover, these precipitates may be decorated with extended dislocations network due to their misfit with silicon lattice and generated stress,<sup>7</sup> leading to even higher recombination activity.

Recently, a method has been reported to deactivate Cu-LID.<sup>8</sup> The method consists of depositing negative corona charges onto both wafer surfaces in order to attract fast-diffusing copper ions from the bulk towards the surface and empty the bulk of copper. However, the only demonstration of the suppression of Cu in the bulk by the above-mentioned method has been a relatively stable effective lifetime under illumination.<sup>8,9</sup> Lifetime methods do not measure copper directly and the effective lifetime consists of both bulk and surface recombination. Therefore, it is necessary to

demonstrate by chemical analysis that copper is indeed influenced by the negative charge and that Cu-LID is a bulk effect instead of mere surface passivation degradation. In this study, we employ Total Reflection X-ray Fluorescence Spectroscopy (TXRF) to investigate the location of copper before and after the removal of Cu-LID. We also perform surface silicon etching before and after the removal of Cu-LID to determine whether the wafer bulk has truly been emptied of copper.

The experiments were performed on six 4-inch boron-doped Cz-Si wafers with the resistivity of  $\sim 3 \Omega\text{-cm}$ , oxygen level of 14 ppma, and thickness of  $\sim 400 \mu\text{m}$ . After standard RCA cleanings and thermal oxidation, the wafers were subjected to following processes depicted in Fig. 1.

In step (i), one wafer was kept as a clean reference, while the rest were intentionally contaminated with copper. The contamination was performed by spin coating 8 ppm of copper solution onto the front surface of the wafers. The wafers were then annealed in nitrogen atmosphere at 800 °C for 20 min to allow copper to diffuse into the bulk. The maximum bulk copper concentration is some  $10^{14} \text{cm}^{-3}$  after in-diffusion anneal.<sup>3</sup>

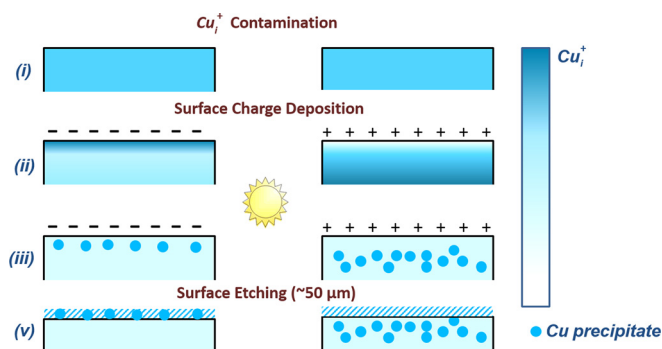


FIG. 1. Distribution of interstitial copper and copper precipitates in oxidized Cz-Si after (i) copper contamination, (ii) negative and positive surface charge deposition, (iii) one-sun illumination, and (v) surface etching.

<sup>a)</sup>Email: yacine.boulfrad@crystals.no

Then, in step (ii) all wafers were charged by  $+0.5 \mu\text{C}/\text{cm}^2$  or  $-0.8 \mu\text{C}/\text{cm}^2$  using the surface corona method. Positive or negative corona charges were deposited onto surfaces of each wafer in order to push/attract  $\text{Cu}_i^+$  ions from/towards the surface, respectively. Cu-contaminated samples were kept in dark for 24 h to allow  $\text{Cu}_i$  to diffuse towards/from the surface, except one negatively charged sample that was processed further immediately after charge deposition.<sup>10</sup> TXRF was used to measure the copper concentration near the surface of the wafers several weeks after corona charge deposition. Copper was detected by TXRF up to  $10 \mu\text{m}$  underneath the surface by tilting the incident beam relative to the sample surface.

Finally, all wafers were cut into two halves for one or more of the following processes: (iii) illumination under a halogen lamp with one sun intensity at room temperature for some 24 h; (iv) annealing on a hot plate at  $200^\circ\text{C}$  for 10 min to deactivate boron-oxygen defects; and (v) etching about  $50 \mu\text{m}$  of both sides of the sample in a  $\text{HNO}_3\text{:HF:CH}_3\text{COOH}$  (75:8:17) solution at  $25^\circ\text{C}$ , followed by deposition of 20 nm layer of  $\text{Al}_2\text{O}_3$  by thermal Atomic Layer Deposition (ALD) at  $100^\circ\text{C}$ , and annealed in nitrogen atmosphere at  $350^\circ\text{C}$  for 30 min. The aim of the silicon etch was to remove the region of accumulated copper near the surface attracted by negative charges [Fig. 1(v)]. All samples were etched in the same batch for comparison. After surface etching, the samples were illuminated and annealed by repeating steps (iii) and (iv).

Minority carrier lifetime was measured after each process step with the quasi-steady-state photoconductance (QSSPC) technique at an injection level of  $\Delta n = 5 \times 10^{15} \text{cm}^{-3}$ . Lifetimes lower than  $30 \mu\text{s}$  were measured at an injection level of  $\Delta n = 5 \times 10^{14} \text{cm}^{-3}$ .

Figure 2 presents the TXRF spectra measured on the negatively and positively charged wafers after step (ii). The copper signal is clear in the negatively charged wafer [Fig.

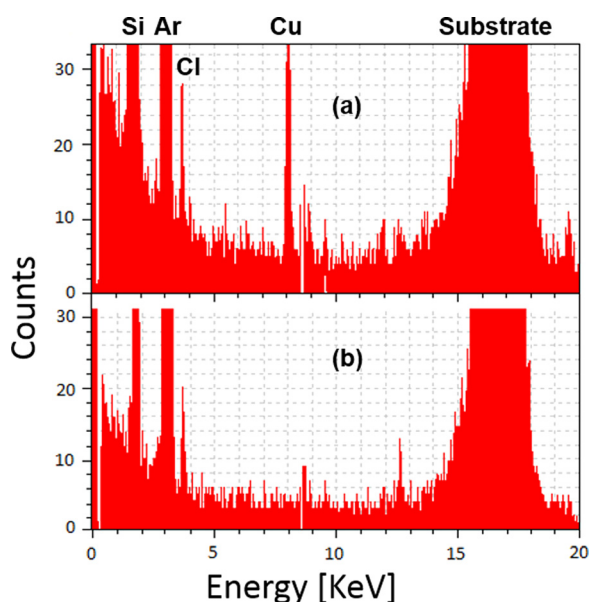


FIG 2. TXRF spectra of two copper-contaminated wafers followed by corona charge deposition with (a) negative charge and (b) positive charge. Ar, Cl, and Si substrate peaks result from the sample preparation and the measurement procedure.

2(a)] measuring a copper surface concentration of  $1.7 \times 10^{13} \text{cm}^{-2}$ , while no copper signal is detected in the positively charged wafer [Fig. 2(b)], suggesting that the copper concentration was well below the detection limit in this sample. These results are a direct proof of copper accumulating near the surface of oxidized Si as a consequence of negative charge deposition, while most of the copper remains in the bulk by electrostatic repulsion due to the surface positive charge.

Figure 3 shows the effective lifetime values of the positively charged samples after several processes. The clean reference sample (blue diamond) shows decrease in lifetime during first illumination due to the formation of BO complexes. The subsequent increase of lifetime after surface etching and the  $\text{Al}_2\text{O}_3$  deposition process is due to the improved passivation quality of  $\text{Al}_2\text{O}_3$  compared to thermal oxide. The second illumination and dark annealing causes expected BO-related lifetime degradation and recovery, respectively.

Unlike BO-LID,  $200^\circ\text{C}$  dark annealing results in significant lifetime degradation in the copper-contaminated sample (green triangle) already before illumination. Ramappa<sup>11</sup> observed similar behavior on Cu-contaminated p-type silicon upon annealing above  $100^\circ\text{C}$ . The diffusion length decrease was attributed to substitutional copper formation through copper complex dissociation,<sup>11</sup> but the lifetime decrease could also be caused by a thermally activated phase transformation of copper into recombination-active copper precipitates at  $200^\circ\text{C}$ .<sup>12</sup>

During illumination, the lifetime dropped drastically in the copper-contaminated sample (black square) due to strong copper-related degradation, which is in agreement with previously reported Cu-LID results.<sup>8,9</sup> After surface etching and  $\text{Al}_2\text{O}_3$  deposition, the lifetime remains very low, even though  $\text{Al}_2\text{O}_3$  provides increased surface passivation. This suggests

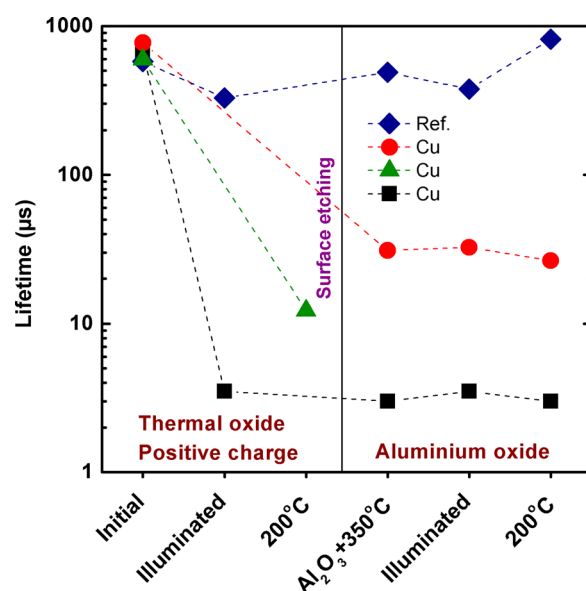


FIG. 3. Average effective lifetime in clean (Ref.) and contaminated (Cu) p-type Cz-Si after different process steps: oxidation and positive corona charge deposition, one-sun illumination at RT, dark anneal at  $200^\circ\text{C}$ , surface etching followed by  $\text{Al}_2\text{O}_3$  deposition at  $100^\circ\text{C}$  and post-anneal at  $350^\circ\text{C}$ , one-sun illumination at RT, and dark anneal at  $200^\circ\text{C}$ .



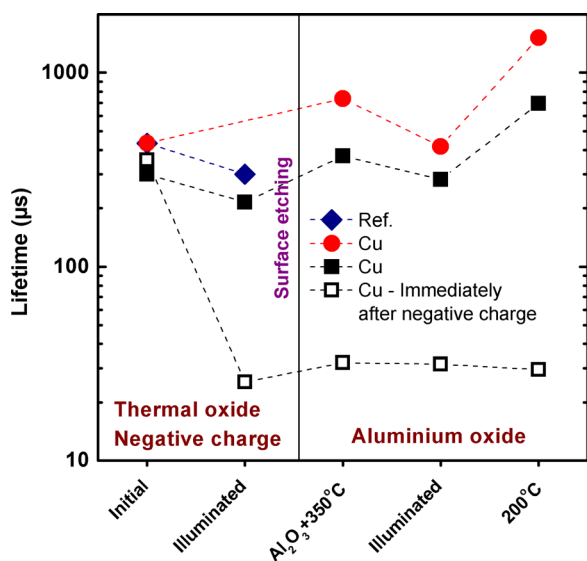


FIG. 4. Average effective lifetime in Cu-contaminated p-type Cz-Si after different process steps: oxidation and negative corona charge deposition, one-sun illumination at RT, surface etching followed by Al<sub>2</sub>O<sub>3</sub> deposition at 100 °C and post-anneal at 350 °C, one-sun illumination at RT, and dark anneal at 200 °C.

that Cu-LID is only weakly sensitive to the surface state and is dominated by recombination in the bulk. As subsequent illumination and annealing had no effect on the lifetime, the light-induced copper precipitates seem to be stable during Al<sub>2</sub>O<sub>3</sub> formation and during the 200 °C anneal.

Another copper-contaminated sample (red circle) was directly subjected to surface etching without prior illumination. Surprisingly, the lifetime drops severely after etching and Al<sub>2</sub>O<sub>3</sub> passivation. However, Al<sub>2</sub>O<sub>3</sub> layer deposition was performed at 100 °C followed by a post anneal at 350 °C for 30 min, and consequently, the drop in the lifetime is most likely attributed to the thermally activated phase transformation of copper similar to the behavior observed after dark anneal at 200 °C.<sup>12</sup>

Figure 4 displays lifetime values of contaminated samples with negative corona charge after similar processes. As concluded from the TXRF results in Fig. 2, interstitial copper has accumulated to the surface of the negatively charged samples. Thus, a relatively high lifetime is maintained after illumination (black square). After surface etching and Al<sub>2</sub>O<sub>3</sub> passivation, the lifetime behaves identically as in the case of the clean reference (shown in Fig. 3), demonstrating further that the negative charge removes copper from the bulk.

Intriguingly, a significant improvement in lifetime was noticed in the sample directly subjected to surface etching without illumination (red circle). The lifetime increase appears to be a result of both enhanced surface passivation and the removal of copper from the material by surface etching. The slightly lower lifetime in the initially illuminated sample is possibly due to some residual copper that was not collected by the initial negative surface charge. During subsequent illumination and annealing, the lifetime behaves again similar to the clean reference sample in Fig. 3. This

indicates that the dominating Cu-LID appears to be eliminated by etching the copper-rich layer near both surfaces.

As mentioned in the experimental part, one copper contaminated sample (open square) was exposed to light right after the negative charge deposition to investigate the effect of copper out-diffusion time after negative charge deposition and to make sure that the negative charge itself is not affecting the surface passivation. As expected, the lifetime drops considerably after immediate illumination. The degraded lifetime is not affected by surface etching, Al<sub>2</sub>O<sub>3</sub> passivation, illumination, or dark annealing. This result indicates that a considerable amount of copper remained in the bulk and precipitated therein during illumination (identical behavior to the positively charged wafers). These results confirm the necessity of a certain out-diffusion time in dark after negative charge deposition to allow copper ions to diffuse near the surface and consequently achieve a copper-free bulk.

In conclusion, this study gives experimental evidence that copper ions accumulate near the wafer surface as a consequence of electrostatic attraction with the deposited negative surface charge. The evidence was twofold: (i) Chemical analysis by means of TXRF revealed copper near the surface of a negatively charged copper-contaminated sample while no copper signal was observed on the positively charged one, (ii) surface etching of the copper-rich surface layer removed permanently Cu-LID.

This research was mainly performed at the Micronova Nanofabrication Centre of Aalto University. The authors acknowledge the financial support of the Finnish Funding Agency for Technology and Innovation, Okmetic Oyj, and SolarWorld Innovations GmbH. The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013)/ERC Grant Agreement No. [307315]. J.L. acknowledges the support of the Finnish Cultural Foundation, the Finnish Society of Electronics Engineers, and the Swedish Academy of Engineering Sciences in Finland (STViF).

<sup>1</sup>J. Schmidt and A. Cuevas, *J. Appl. Phys.* **86**, 3175 (1999).

<sup>2</sup>K. Bothe and J. Schmidt, *Appl. Phys. Lett.* **87**, 262108 (2005).

<sup>3</sup>H. Savin, M. Yli-Koski, and A. Haarahiltunen, *Appl. Phys. Lett.* **95**, 152111 (2009).

<sup>4</sup>R. Sachdeva, A. A. Istratov, and E. R. Weber, *Appl. Phys. Lett.* **79**, 2937 (2001).

<sup>5</sup>A. A. Istratov, H. Hedemann, M. Seibt, O. F. Vyvenko, W. Schröter, T. Heiser, C. Flink, H. Hieslmair, and E. R. Weber, *J. Electrochem. Soc.* **145**, 3889 (1998).

<sup>6</sup>A. A. Istratov and E. R. Weber, *J. Electrochem. Soc.* **149**, G21 (2002).

<sup>7</sup>K. Graff, *Metal Impurities in Silicon-Device Fabrication* (Springer, 2000).

<sup>8</sup>J. Lindroos, M. Yli-Koski, A. Haarahiltunen, and H. Savin, *Appl. Phys. Lett.* **101**, 232108 (2012).

<sup>9</sup>Y. Boulfrad, J. Lindroos, A. Inglese, M. Yli-Koski, and H. Savin, *Energy Procedia* **38**, 531 (2013).

<sup>10</sup>H. Väinölä, M. Yli-Koski, A. Haarahiltunen, and J. Sinkkonen, *J. Electrochem. Soc.* **150**, G790 (2003).

<sup>11</sup>D. A. Ramappa, *Appl. Phys. Lett.* **76**, 3756 (2000).

<sup>12</sup>A. Cros, M. O. Aboelfotoh, and K. N. Tu, *J. Appl. Phys.* **67**, 3328 (1990).